

Section XXXX Standard Operating Procedures for Lead (Pb) Mass Audit

1. Scope & Applicability

The purpose of this SOP is to provide guidance for the audit of the Lead (Pb) analytical reference method. These procedures are applicable for Pb analytical operations in Missouri.

Based on its review of the air quality criteria and national ambient air quality standards (NAAQS) for lead (Pb), EPA has made revisions to the NAAQS for Pb. EPA has revised the primary standard level to $0.15 \mu\text{g}/\text{m}^3$, from the previous standard of $1.5 \mu\text{g}/\text{m}^3$. EPA is retaining the current indicator of Pb in total suspended particles (Pb-TSP).

The new NAAQS for lead (Pb) and its compounds, 0.15 micrograms per cubic meter, is an arithmetic mean concentration accumulated over a 3-month period. The concentration of Pb in the atmosphere is determined in the total volume of air sampled and is expressed as a mass per cubic meter ($\mu\text{g}/\text{m}^3$) at local temperature and pressure conditions.

The Code of Federal Regulations (40 CFR part 58 Appendix A) details the Quality Assurance Requirements for NCore and PSD Air Monitoring. This includes Pb air monitoring. To assess measurement uncertainty, monitoring organizations shall institute a Pb mass quality assurance program that involves the preparation of Pb audit filters. This represents an independent assessment of data quality. This is intended to be an independent and blind procedure aimed at laboratories conducting Pb analyses of filters from air samplers.

The CFR requires an independent quarterly audit of the Pb analysis procedures. Due to the Missouri SIP, it is also necessary to have uniform audits of all analytical labs in the Missouri network that analyze Pb filters. For these reasons, Missouri is conducting a quarterly Pb audit strip program.

There are two primary objectives of the Missouri Pb audit strip program. The first is to provide a precision and bias estimate for the Pb analytical process in the Missouri Pb sampling network. The second objective is to provide a means to compare network laboratories and identify individual laboratories that may need to reevaluate quality control procedures.

2. Summary of Method

The following information is taken from 40 CFR part 58 Appendix A: Quality Assurance

Requirements for NCore and PSD Air Monitoring, Section 3.3.3: *Pb Quality Assurance Methods* and Section 3.3.4.2 *Pb Analysis Audits*.

Each calendar quarter or sampling quarter (PSD), an audit of the Pb reference method analytical procedure should be performed using glass fiber filter strips containing a known quantity of Pb. These audit sample strips are prepared by depositing a Pb solution on unexposed TSP glass fiber filter strips of dimensions 1.9cm by 20.3cm and **allowing them to dry thoroughly. The audit samples must be prepared using batches of reagents different from those used to calibrate the Pb analytical equipment being audited. Audit samples must be extracted using the same extraction procedure used for exposed filters.** Each quarter that field samples are analyzed, three audit samples in each of the two ranges should also be analyzed. The audit sample analyses shall be distributed as much as possible over the entire calendar quarter.

Prepare audit samples in the following concentration ranges: Range 1 is 30–100% of the Pb NAAQS (equivalent ambient Pb concentration, $\mu\text{g}/\text{m}^3$). Range 2 is 200–300% of Pb NAAQS. The NAAQS is 0.150 $\mu\text{g}/\text{m}^3$ of Pb in ambient air. The entire audit range is 0.045 $\mu\text{g}/\text{m}^3$ to 0.450 $\mu\text{g}/\text{m}^3$.

The audit guidance specifies an ambient concentration rather than a mass per filter strip criteria. This means that assumptions must be made related to the typical flow rate of the Pb samplers, if the analysis instrument is to be audited at the proper location on the analytical range. A median value of 1.39 m^3/min (2000 m^3) could be chosen, but a better decision must be made based on typical flow rates in the actual network of samplers.

Missouri will soon implement an upgrade to the TSP samplers by replacing the brushless motor electrical flow control system (variac) with a critical venturi (Wedding VFC) flow control systems. The new system will most likely result in a mean ambient flow rate closer to 1.2 m^3/min (1728 m^3 volume). This is most likely the volume that will be used to calculate the filter strip concentrations for auditing the Pb analysis procedure.

The location of a sample in the analytical range is also a function of the dilution (digestion) volume of acid solution used to recover the analyte from the glass TSP filter. Currently EPA specifies 50 mL of acid digestion, although 100 mL is also used by some laboratories. 25 micrograms deposited on an audit strip will show up on the analysis instrument range at either 0.500 $\mu\text{g}/\text{mL}$ (mg/L) or 0.250 $\mu\text{g}/\text{mL}$ depending on the amount of acid used for digestion of each strip.

3. Definitions and Acronyms

See section 1030 of this manual.

4. Health and Safety Warnings

See section 1080 of this manual. For information on the potential hazards of Pb or HNO₃, refer to the appropriate MSDS.

5. Cautions

NA

6. Interferences

NA

7. Personnel Qualifications/Training

See section 1060 of this manual.

8. Equipment and Supplies

A) Glassware

A Pyrex Borosilicate Glass 500 mL Volumetric Flasks with plastic caps will be used.

A known mass of Pb standard solution will be diluted in a 500 mL flask. Only Class A, volumetric flasks, with a known uncertainty and individual serial numbers, will be used. These are certified NIST-traceable according to ASTM E288 with documented measurement uncertainties. The volumetric flasks will be rinsed and cleaned with de-ionized water only.

B) Deionized Water

The lab water purification system consists of particulate filters, activated charcoal, cation resin bed, anion resin bed, mixed (cation / anion resin) bed, and a unibed (sorbent filter material). This purified water will simply be referred to as deionized water. All water for Pb solutions should be drawn from the weigh-room de-ionized water tap. Blank filters will be dosed with deionized water and analyzed to verify that water does not contribute Pb. Glassware will be cleaned only with deionized water until the water sheets evenly on the glassware, and does not bead or break.

C) Filter Strips

Preparation of the filter strips involves cutting up an unexposed **glass** fiber filter into strips measuring 0.75 inch wide by 8.0 inches long (1.9 cm by 20.3 cm). A plastic ruler and a razor blade cleaned with alcohol will be used for this. A clean cutting board is also used. Blank filter strips (with no water or solution added) will be analyzed to verify that the filter material does not contribute Pb. EPA Region 7 provides the glass fiber filters and should be contacted if the supply is low. The filter strips will be stored in desiccating chambers (with desiccant trays and strip holding

racks/clips). The strips will be placed in plastic sample bags with labels to await distribution.

D) Pb Stock Solutions

The master standard is a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM no. 3128) for Lead (Pb). This has a 0.2% expanded uncertainty associated with the certified concentration. SRM 3128 is intended for use as primary calibration standard for the quantitative determination of Pb, specifically by ICP-MS (inductively-coupled plasma mass spectrometry). Missouri's Pb mass audit is designed around the NIST SRM. The SRM is only offered in one concentration. One unit of SRM 3128 consists of five 10 mL sealed borosilicate glass ampoules of an acidified aqueous solution prepared gravimetrically to contain a known mass fraction of Pb (nominally 10 mg/g). The aqueous solution contains nitric acid [HNO₃] at a volume fraction of approximately 10 %, Lead Nitrate [Pb(NO₃)₂] by mass fraction of 1.6 %, Pb by mass fraction of 1.0 %. Missouri will follow NIST's recommended method for preparing standard stock solutions. All stock solutions will be directly prepared from the SRM, **not** serially diluted from a master stock solution.

E) Microbalance

A Mettler Toledo AJ100 balance is used. It has a resolution of 0.0001 grams or 0.1 mg. It is certified annually resulting in a precision of +/- 0.2 mg (0.0002 g). This is performed with NIST-traceable mass standards. The mass of SRM solution entering into the calculations will be determined on this balance. A 1 oz (30mL) widemouth polyethylene bottle will be used as the weighing vessel.

F) Pipetter

To dose filter strips, a BIOHIT fixed-volume pipetter (500 micro-Liter) with disposable pipet tips is used. The filter strips will be spiked with **0.5 mL** of stock solution while the strip is hanging from a chromatography clip on a Teflon rod. The spike will be dispensed with a single-channel BIOHIT Pro-line mechanical pipetter with a fixed volume of 500 micro-liters (0.5 mL). The pipetter uses clean disposable pipet tips. The pipetter is certified by the manufacturer per ISO 8655.

9. Installation and Calibration of Equipment

Prior to mass determinations, the balance must be calibrated. All data and calculations required for these activities are to be recorded and filed. There is an example stock standard preparation form attached to end of the SOP.

Balance Calibration and Verification:

Make sure the balance is level. Turn on the balance (Mettler AJ100) by pushing the bar down. Note: to turn "off," lift bar up. Hold bar down until "CAL" appears on screen. Place the 100-gram mass standard on balance and close enclosure. Wait for "0" to appear then remove the 100-gram mass standard. After a brief period, place the 5-gram mass standard on the balance. It must read

within 5.0000 +/- 0.0005 (4.9995 – 5.0005) grams. If not, recalibrate. Then place the 1-gram mass standard on the balance. It should also read within the specifications.

10. Operating Procedures

Filter Strip Preparation:

Clean a razor blade with alcohol. Use the clean plastic forceps to fold an unexposed glass fiber filter in half length-wise, and place it on a plastic cutting board. Using the plastic ruler as a template, cut the filter into strips measuring 0.75 inch wide by 8.0 inches long (1.9 cm by 20.3 cm). Use the “clean” plastic forceps to unfold each strip and hang it from a clip on the Teflon rod. Cut strips should be stored in the “clean” closed chamber until ready for dosing.

Stock Solution Preparation:

Place an empty, dry 30-mL widemouth polyethylene (PE) bottle (without cap) on the microbalance. Record the “bottle mass.” This is usually about 7.8 grams without the cap. Carefully break one 10-mL ampoule of SRM 3128. Using the equation in the calculations section, calculate how much SRM is needed to achieve the desired Pb strip concentration. Pour in a little more than the necessary mass of SRM to the PE bottle. Record the “total mass.” Pour remaining SRM in ampule into a second pre-weighed PE bottle for later use. Carefully pour the contents of the PE bottle into a 100-mL volumetric flask. Immediately place the PE bottle back on the balance **without rinsing**. Record the “remainder mass.” Rinse the inside surfaces of the flask with deionized water until the water level gets close to the mark. The deionized water should always come from weigh room deionized water tap. Slowly finish filling to the mark with deionized water. The bottom of the meniscus should be touching the flask mark. Place the plastic cap on the flask. Properly mix the stock solution by inverting the flask repeatedly.

Concentration Determination:

Calculate the concentration of stock solution in the flask. EQUATION: Total Bottle Mass - Remainder Mass = Final Mass of SRM added to flask. Multiply this by the SRM concentration (~10g/g) and divide by the flask volume. This results in a mass per volume concentration of Pb for the stock solution.

Dosing of Filter Strips:

Properly mix the stock solution in the capped volumetric flask. Pour the contents of the flask into a labeled wide-mouth glass sample jar. Use the wide-mouth graduated glass jars with Teflon-lined lids. This allows the use of the manual pipetter (with pipetter tips). Each new pipette tip must be conditioned five times with solution, before spiking. The pipette manual has directions for the proper conditioning and use of micro-pipette. Transfer 0.5 milliliter (**0.5 mL**) of audit Pb solution to prepared strips of glass filter. Strips should be held by plastic chromatography clips suspended on a Teflon rod, on a rod-holding rack. Grip the bottom of the strip using the “exposed” plastic forceps. Hold the strip out at a steep angle to apply solution. Do not use the “clean” plastic forceps

for this part of the procedure. Carefully observe the strip while adding the stock solution to ensure all is absorbed. The solution should be evenly dispensed over the filter, starting at the top of the filter. The micro-pipette must be held vertically at all times. Work quickly to spike the strips from the jar to avoid potential evaporation effects. Move the rod (with 6 clips and hanging strips) to a drying (desiccating) chamber rack. Place the micro-pipette in the vertical holder when not spiking strips. The chambers hold 7-8 rods with 6 strips per rod.

Make sure the desiccant in the chamber is fresh. The filters should be dried for several days. Use the “exposed” forceps to handle filters at this stage. Carefully remove each strip from the clip using only the forceps to touch the strip. Fold the strip carefully in half, with the dosed surface to the inside, taking care not to touch the dosed surface. Immediately place each folded strip in a separate labeled plastic sample bag to await distribution. Label the bag with a code indicating the concentration. If desired, each bag (with a single strip) may be labeled with a unique identification number.

11. Maintenance Procedures

These procedures include checking the micro-pipetter filter occasionally and replacing it. The balance must also be kept clean. Desiccant must be prepared for every batch. Periodically verify that the deionized water system components are being maintained properly. All glassware must be thoroughly washed with deionized water immediately after every use.

12. Troubleshooting

Refer to the balance or pipette manufacturer’s manual if troubleshooting is necessary.

13. Quality Control Procedures

Each SRM batch is purchased directly from NIST with a documented certified concentration and uncertainty.

Each Class A volumetric flask has an individual serial number. These are certified NIST-traceable according to ASTM E288 (using NIST-traceable weights) with documented measurement uncertainties. ASTM E288 sets limits on the maximum standard uncertainty of 500.00 +/- 0.16 mL.

The micro-pipette has a documented certified uncertainty upon purchase. Use the single-channel BIOHIT Pro-line mechanical pipetter with a fixed volume of 500 uL. The pipetter is certified by the manufacturer per ISO 8655. This guideline limits the uncertainty at 500 uL to better than +/- 4 uL. EPA NPAP procedures also use a 0.5 mL (500 uL) spike.

The Mettler Toledo AJ100 balance has a resolution of 0.0001 grams or 0.1 mg. It is certified

annually resulting in a precision of +/- 0.2 mg. The balance must be calibrated with 100 gram mass before each use. It is recommended that the operator perform the QC check with the 5 gram mass and 1 gram mass before each measurement of SRM mass. The mass standards are certified traceable to NIST weights on an annual basis. The certification documents for both the balance and the mass standards are retained in the laboratory.

Each time a new batch of SRM is used, perform a set of repeated micro-pipette trials using the microbalance. These trials will serve to verify both balance and micro-pipette performance. This will also provide a value for uncertainty components in the procedure. Use the pipette to place 0.5 mL volumes into a widemouth polyethylene bottle and record the mass change each time for a predetermined number of repetitions. The mass change for 0.5 mL should be approximately 0.5 gram. Calculate the standard deviation.

14. Calculations

Audit strip concentration determination (nominal values):

$$(x.xxxx_g_SRM) \left(\frac{10.000_mg_Pb}{grams_SRM} \right) \left(\frac{1_flask}{500_mL} \right) \left(\frac{1000\mu g}{mg} \right) \left(\frac{0.50mL_pipet}{filter_strip} \right) = \frac{xxx_μg_Pb}{filter_strip}$$

NOTE: with each SRM there is about 50 mL of total solution resulting in slightly more than 50 grams of solution available for use to make the standard solutions.

Example 1:

$$(2.00_g_SRM) \left(\frac{9.987_mg_Pb}{g_SRM_solution} \right) \left(\frac{1}{500mL_flask} \right) \left(\frac{1000\mu g}{mg} \right) \left(\frac{0.50mL_pipet}{filter_strip} \right) = \frac{20.0_μg}{strip}$$

Example 2:

$$(0.50_g_SRM) \left(\frac{9.987_mg_Pb}{g_SRM_solution} \right) \left(\frac{1}{500mL_flask} \right) \left(\frac{1000\mu g}{mg} \right) \left(\frac{0.50mL_pipet}{filter_strip} \right) = \frac{5.0_μg}{strip}$$

Example 3:

$$(6.50_g_SRM) \left(\frac{9.987_mg_Pb}{g_SRM_solution} \right) \left(\frac{1}{500mL_flask} \right) \left(\frac{1000\mu g}{mg} \right) \left(\frac{0.50mL_pipet}{filter_strip} \right) = \frac{64.9_μg}{strip}$$

Statistics and Uncertainty Calculation for Audit Method:

The main components of uncertainty in the audit process (audit concentration) are:

$$(2.0000 \text{ _g _SRM}) \left(\frac{10.000 \text{ _mg _Pb}}{\text{gram _SRM}} \right) \left(\frac{1 \text{ _flask}}{500.00 \text{ _mL}} \right) \left(\frac{0.50 \text{ _mL _pipet}}{\text{filter _strip}} \right) = \frac{0.020 \text{ _mg}}{\text{strip}} = \frac{20 \text{ _}\mu\text{g}}{\text{strip}}$$

1) Uncertainty in the mass of SRM obtained on the microbalance. This uncertainty arises from the calibration and repeatable measurement error of the laboratory balance. This will be determined from the resolution of the balance (0.1 mg or 0.0001 g), repeated weighing of the calibration weight, and the annual calibration certification documentation.

Standard uncertainty estimate: +/- 0.002 g which is approximately 0.1 % or 1000 ppm.

2) Uncertainty in the SRM concentration. This is determined by NIST and is known to be 0.2% (at a 95% uncertainty level). Example: 9.987 mg/g +/- 0.018 mg/g. The standard uncertainty is half the expanded uncertainty.

Standard uncertainty estimate: nominal 0.010 mg/g which is 0.1 % or 1000 ppm (relative uncertainty).

3) Uncertainty in the volume of the dilution flask. Class A glass flasks are shipped from the manufacturer with NIST traceable uncertainty documentation. The document covers the type B uncertainty which will vary depending on the flask volume (500.00 +/- 0.16 mL). The user error uncertainty (type A) will be evaluated with repeated weighings (using 0.5 ml H₂O = 0.5 gram).

Relative Standard Uncertainty Estimate: +/- 0.5 % or 5000 ppm

4) Uncertainty in the volume measurement of the pipet and the delivery process. The pipetter is shipped from the manufacturer with NIST traceable uncertainty documentation. ISO 8655 sets a limit on the maximum standard uncertainty of 0.40%. The document covers the type B uncertainty. Example: actual mean of 0.5021 mL +/- 0.0020 mL. The user error uncertainty (type A) will be evaluated with repeated weighing trials with different tips (using 1 ml H₂O = 1 gram).

Standard uncertainty estimate: 0.500 mL +/- 0.005 mL which is 1% or 10000 ppm.

Using the estimates of the elemental uncertainties above and evaluating them in the context of the process equation produces an overall combined uncertainty for the process. The normalized uncertainties are combined in the standard method (square root of the sum of squares) using a simplified method (relative standard uncertainties) of expressing the sensitivity coefficients.

$$(10.000 \text{ _g _SRM}) \left(\frac{10.000 \text{ _mg _Pb}}{\text{g _SRM _solution}} \right) \left(\frac{1}{100\text{mL _flask}} \right) \left(\frac{1.0\text{mL _pipet}}{\text{filter _strip}} \right) = \frac{1.000 \text{ _mg}}{\text{strip}}$$

$$\frac{u_{conc}}{Conc} = \sqrt{\left(\frac{u_{SRM}}{SRM}\right)^2 + \left(\frac{u_{mass}}{mass}\right)^2 + \left(\frac{u_{vol}}{vol}\right)^2 + \left(\frac{u_{pipet}}{pipet}\right)^2}$$

$$\frac{u_{conc}}{Conc} = \sqrt{(0.001000)^2 + (0.001000)^2 + (0.005000)^2 + (0.010000)^2}$$

$$\frac{u_{conc}}{Conc} = 0.011269 = 1.127\%$$

This is the combined standard uncertainty. Using a coverage factor of 2, the expanded (95%) uncertainty estimate is **2.25%**.

15. Data Acquisition and Data Reduction

See Section 1450 of this manual.

16. Computer Hardware and Software

See Section 1450 of this manual.

17. Data and Records Management

See Section 1460 of this manual.

18. Quality Assurance Procedures

Missouri plans to send U.S. EPA Region 7 Laboratory filter strips to validate the procedure and calculations, **not** to provide the actual audit concentrations. Each quarter, U.S. EPA Region 7 will analyze strips as the benchmark laboratory. If the calculated value differs across all audit levels by more than 10%, strip preparation procedures will be re-evaluated.

If the calculated (estimated) mass per filter, for each audit level, exceeds the 95% CI (1.96 x stdev) of the sample mean of all the laboratory analysis results, then Missouri staff will investigate for possible problems in the filter strip procedure. This is with the condition that the standard deviation of the sample mean is less than 5% of the mean.

Missouri staff will also have EPA Region 7 randomly analyze larger batches of filters for quality

control. 20 filters will be randomly selected for analysis from a single concentration level. A 95% recovery and 2% CV is desired.

Also, batches of blank filter strips dosed with 0.5 mL of deionized water, as well as blank filters with no solution or water added will be occasionally submitted for analysis. Batches of blank filter strips (with no water or solution added) will be randomly analyzed to verify that the filter material does not contribute Pb.

19. Procedures for Evaluation of Audit Results

There are two objectives of the Missouri Pb audit strip program. The first is to provide a precision and bias estimate for the Pb analytical process in the Missouri Pb sampling network. The second objective is to provide a means to compare network laboratories and identify individual laboratories that may need to reevaluate quality control procedures.

To accomplish the first objective, audit results will be calculated and evaluated according to the guidance issued in 40 CFR Part 58, Appendix A, section 4.4 "Statistics for the Assessment of Pb." Section 4.1.3, of 40 CFR Part 58 Appendix A, contains the guidance for the Pb strip laboratory bias assessment.

40 CFR Part 58 Appendix A, section 3.3.4.2 *Pb Analysis Audits*, states;

(c) Report the audit concentrations (in $\mu\text{g Pb/filter or strip}$) and the corresponding measured concentrations (in $\mu\text{g Pb/filter or strip}$) using AQS unit code 077. The [relative] percent differences [RPD] between the concentrations are used to calculate analytical accuracy as described in section 4.1.3 of this appendix.

Section 4.1.3 Bias Estimate states;

The bias estimator is an upper bound on the mean absolute value of the percent differences as described in equation 3 of this section:

Equation 3

$$\text{abs BIAS} = AB + t_{0.95, n-1} * [AS/\text{sqrt}(n)]$$

n is the number of single point checks being aggregated;

$t_{0.95, n-1}$ is the 95th quantile of a t-distribution with $n-1$ degrees of freedom;

AB is the mean of the absolute values of the di 's (RPD's) and is calculated using equation 4 of this section:

Equation 4

$$AB = (1/n) * [\text{sum of all abs}(d)]$$

d = RPD

AS is the standard deviation (stdev) of the absolute value of the d_i 's and is calculated using equation 5 of this section:

Equation 5

AS= stdev of all abs(d)

To accomplish the second objective, the audit data will be scrutinized further. An initial target is that the sample mean will fall within 5% of the calculated (estimated) value. Another target is for the standard deviation (STDEV) of the sample to be less than 5% of the sample mean. Also, all samples should fall within 2 times the STDEV of the sample mean. Finding potential outliers is important for identifying labs that may need compliance assistance. An outlier may be defined as any value that differs from the next nearest value by an amount similar to the entire range encompassing the rest of the values.

20. References

40 CFR, Part 58, Appendix A, (Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS)).

40 CFR, Part 50, Appendix G, (Method for the Determination of Lead in Suspended Particulate Mater Collected from Ambient Air).

NPAP-SOP-015. Lead (Pb) Audit. B.J. Carpenter, K. Rufty. ManTech Environmental Technology, Inc. RTP, NC. 15 May 1998

NIST SRM Lead Standard Solution certificate of analysis and guidance document (SRM 3128). July 2007. (Explains standard solution preparation). NIST SRM #3128 "instructions for use" for "Preparation of Working Standard Solutions by Volume." This is the National Institute of Standards and Technology Standard Reference Material Lead (Pb) solution

Quality Assurance Requirements for NCore and PSD Air Monitoring.

40 CFR part 58, Appendix A.

Section 3.3.3 Pb Methods

3.3.3.2 Pb Strips (preparation)

4.4 Statistics for the Assessment of Pb

4.4.2.2 Lead strip calculations

Mettler J-Series Balance operating manual.

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Reference ISO 8655 which specifies the general requirements for piston-operated volumetric apparatus.

Reference ASTM E288 for certification requirements of volumetric flasks.

ADDENDUM

Example audit strip concentration determination during preparation:

$$(2.42 \text{ _g _SRM}) \left(\frac{10.000 \text{ _mg _Pb}}{\text{grams _SRM}} \right) \left(\frac{1 \text{ _flask}}{500.00 \text{ _mL}} \right) \left(\frac{0.50 \text{ _mL _pipet}}{\text{filter _strip}} \right) = \left(\frac{24.2 \text{ _}\mu\text{g _Pb}}{\text{filter _strip}} \right)$$

Calculations for the comparison of audit levels to actual Ambient Concentrations:

The purpose of this exercise is to gauge whether the audit levels provided to the labs are actually challenging the data quality at a relevant regulatory level.

The audit guidance specifies an ambient concentration rather than a mass per filter strip criteria. This means that assumptions must be made related to the typical flow rate of the Pb samplers. Pb samplers are allowed to flow 1.1 to 1.7 m³/min (ambient conditions). Over 24 hours, volume at 1.1 m³/min is 1584 m³. For 1.7 m³/min, volume is 2448 m³. An audit strip with 25 micrograms of Pb (300 micrograms per TSP filter) could represent an ambient air concentration of 0.123 to 0.189 ug/m³, depending on the air volume chosen. A median value of 1.39 m³/min (2000 m³) could be chosen, but a better decision must be made based on typical flow rates in the actual network of samplers.

Missouri will use TSP samplers with a critical venturi (Wedding VFC) flow control systems, with a mean ambient flow rate closer to 1.2 m³/min (1728 m³ volume). This volume is used to calculate the filter strip concentrations for auditing the Pb analysis procedure.

The calculation below uses a “real” sample filter strip with an arbitrary content of 20 micrograms per strip of Pb. The analytical lab receives the exposed filter, cuts up the filter, and performs a digestion on each of the 12 strips. The acid digestion volume is 50 mL resulting in an analyte solution submitted for analysis. The analysis result is reported in mg/L or the equivalent micrograms/mL.

$$\left(\frac{20.0 \text{ _}\mu\text{g _Pb}}{\text{strip}} \right) \left(\frac{1 \text{ _mg}}{1000 \text{ _}\mu\text{g}} \right) \left(\frac{1 \text{ _strip}}{50 \text{ _mL _analyte}} \right) \left(\frac{1000 \text{ _mL}}{1 \text{ _Liter}} \right) = \frac{0.40 \text{ _mg _Pb}}{\text{L _analyte}}$$

Here 0.40 mg/L is the result of this analysis. The lab then calculates the total mass of Pb per whole filter:

$$\left(\frac{0.40_mg_Pb}{L_analyte}\right)\left(\frac{1_Liter}{1000_mL}\right)\left(\frac{50_mL_analyte}{strip}\right)\left(\frac{1000_ug}{mg}\right)\left(\frac{12_strips}{TSP_filter}\right) = \frac{240_ug}{TSP_filter}$$

The sampling air volume is then used to determine an ambient concentration. The air volume estimate is based on typical sampling, with 20.3x25.4cm (8x10inch) filter, at **1.20 m³/min**, for 24 hours, resulting in approximately **1728 m³** volume.

$$\left(\frac{1.20_meter^3}{minute}\right)\left(\frac{60_minutes}{1_hour}\right)\left(\frac{24_hours}{filter_run}\right) = \frac{1728_meter^3}{TSP_filter}$$

Ambient concentration calculation:

$$\left(\frac{240_ug}{filter}\right)\left(\frac{1_filter}{1728_m^3}\right) = \frac{0.140_ug}{meter^3}$$

EXAMPLE NAAQS CALCULATION

$$\left(\frac{0.150_ug}{meter^3}\right)\left(\frac{1728_m^3}{1_TSP_filter}\right)\left(\frac{1_TSP_filter}{12_filter_strips}\right) = \frac{21.6_ug}{filter_strip}$$

$$\left(\frac{21.6_ug_Pb}{strip}\right)\left(\frac{1_mg}{1000_ug}\right)\left(\frac{1_strip}{50_mL_digestion}\right)\left(\frac{1000_mL}{1_Liter}\right) = \frac{0.432_mg_Pb}{L_analyte}$$

Here 0.432 mg/L is the result of the analysis, as it would be reported in the Missouri LIMS system.

The audit samples are to be prepared in following ranges; 30% to 300% of the 2009 NAAQS for Pb, which is 0.150 ug/m³ of Pb in ambient air. This is 0.045 ug/m³ and 0.450 ug/m³.

$$\left(\frac{0.045_ug}{meter^3}\right)\left(\frac{1728_m^3}{1_TSP_filter}\right)\left(\frac{1_TSP_filter}{12_filter_strips}\right) = \frac{6.5_ug}{filter_strip}$$

$$\left(\frac{0.450_ug}{meter^3}\right)\left(\frac{1728_m^3}{1_TSP_filter}\right)\left(\frac{1_TSP_filter}{12_filter_strips}\right) = \frac{64.8_ug}{filter_strip}$$

Comparison of audit levels to QC controls:

The purpose of this exercise is to gauge whether the audit levels provided to the labs are actually challenging the analytical instrument at levels that are representative of typical analytical results. It is also important that some audit levels are close to the levels of the internal QC controls.

The analysis result estimate is based on the ICP-OES analytical range of 0.00-50.00 ug/mL (same as mg/L). Typical analytical Pb QC controls are at 1.0 ug/mL and 5.0 ug/mL. There is also a PQL sample at 0.1 ug/mL.

The location of a sample in the analytical range is also a function of the dilution (digestion) volume of acid solution used to recover the analyte from the glass TSP filter. Currently EPA specifies 50 mL of acid digestion, although 100 mL is also used. 25 micrograms per audit strip will show up on the analysis instrument range at either 0.500 ug/mL (mg/L) or 0.250 ug/mL depending on the amount of acid used for digestion of each strip. **This will depend on the result of EPA ORD's investigations and issued guidance related to the analysis procedures. Currently, Missouri's analytical procedure will use 50 mL of acid.** A good reference for this may be the 2007 CARB SOP for trace metal analysis for ambient air particulate matter using ICP-MS.

$$\left(\frac{0.150 \text{ } \mu\text{g}}{\text{meter}^3} \right) \left(\frac{1728 \text{ } m^3}{1 \text{ } TSP \text{ } filter} \right) \left(\frac{1 \text{ } TSP \text{ } filter}{12 \text{ } filter \text{ } strips} \right) = \frac{21.6 \text{ } \mu\text{g}}{\text{filter } strip}$$

$$\left(\frac{21.6 \text{ } \mu\text{g } Pb}{strip} \right) \left(\frac{1 \text{ } mg}{1000 \text{ } \mu\text{g}} \right) \left(\frac{1 \text{ } strip}{50 \text{ } mL \text{ } digestion} \right) \left(\frac{1000 \text{ } mL}{1 \text{ } Liter} \right) = \frac{0.43 \text{ } mg \text{ } Pb}{L \text{ } analyte}$$

Here 0.43 mg/L is the result of this analysis, as it would be reported in the Missouri LIMS system.

$$\left(\frac{0.045 \text{ } \mu\text{g}}{\text{meter}^3} \right) \left(\frac{1728 \text{ } m^3}{1 \text{ } TSP \text{ } filter} \right) \left(\frac{1 \text{ } TSP \text{ } filter}{12 \text{ } filter \text{ } strips} \right) = \frac{6.5 \text{ } \mu\text{g}}{\text{filter } strip}$$

$$\left(\frac{6.5 \text{ } \mu\text{g } Pb}{strip} \right) \left(\frac{1 \text{ } mg}{1000 \text{ } \mu\text{g}} \right) \left(\frac{1 \text{ } strip}{50 \text{ } mL \text{ } digestion} \right) \left(\frac{1000 \text{ } mL}{1 \text{ } Liter} \right) = \frac{0.13 \text{ } mg \text{ } Pb}{L \text{ } analyte}$$

Missouri's PQL for ICP-OES method is 0.1 mg/L Pb.

$$\left(\frac{0.450 \text{ } \mu\text{g}}{\text{meter}^3} \right) \left(\frac{1728 \text{ } m^3}{1 \text{ } TSP \text{ } filter} \right) \left(\frac{1 \text{ } TSP \text{ } filter}{12 \text{ } filter \text{ } strips} \right) = \frac{64.8 \text{ } \mu\text{g}}{\text{filter } strip}$$

$$\left(\frac{64.8 \text{ } \mu\text{g} \text{ } Pb}{\text{strip}}\right)\left(\frac{1 \text{ } mg}{1000 \text{ } \mu\text{g}}\right)\left(\frac{1 \text{ } strip}{50 \text{ } mL \text{ } digestion}\right)\left(\frac{1000 \text{ } mL}{1 \text{ } Liter}\right) = \frac{1.30 \text{ } mg \text{ } Pb}{L \text{ } analyte}$$

Currently, the lowest calibration point for Missouri’s ICP-OES is 1.0 mg/L Pb.

It will be challenging to reach the lowest levels required by the audit guidance while also maintaining the high end of the analysis range (25.00 or 50.00 mg/L Pb) to successfully meet the needs of Missouri’s network and SIP obligations.

Typical Missouri sample analysis results (using 50 mL analyte) range from 4-10 mg/L with occasional values at 20 mg/L, and rare upper values of 30 mg/L.

$$\left(\frac{100 \text{ } \mu\text{g} \text{ } Pb}{\text{strip}}\right)\left(\frac{1 \text{ } mg}{1000 \text{ } \mu\text{g}}\right)\left(\frac{1 \text{ } strip}{50 \text{ } mL \text{ } analyte}\right)\left(\frac{1000 \text{ } mL}{1 \text{ } Liter}\right) = \frac{2.0 \text{ } mg \text{ } Pb}{L \text{ } analyte}$$

$$\left(\frac{1000 \text{ } \mu\text{g} \text{ } Pb}{\text{strip}}\right)\left(\frac{1 \text{ } mg}{1000 \text{ } \mu\text{g}}\right)\left(\frac{1 \text{ } strip}{50 \text{ } mL \text{ } analyte}\right)\left(\frac{1000 \text{ } mL}{1 \text{ } Liter}\right) = \frac{20.0 \text{ } mg \text{ } Pb}{L \text{ } analyte}$$

NPAP Lead (Pb) Audit Strip
STOCK SOLUTION PREPARATION FORM

CODE:

Date: _____

Solution Prepared by: _____

NIST SRM 3128 (Lead Standard Solution) Lot Number: _____

NIST SRM Certified Value of Lead (in mg/g): _____

NIST SRM Uncertainty (in mg/g): _____

Balance model: _____

Balance Serial Number: _____

Balance Certification Date: _____

Balance Certified Uncertainty (or Precision): _____

Balance Calibration Mass (in grams): _____

Balance Reading of Standard Reference Mass (in grams): _____

Flask Volume (milliliters): _____

Volumetric Flask Serial Number: _____

Flask Certified Uncertainty (or precision): _____

Example Calculation:

$$(2.000_g_SRM_add_to_flask) \left(\frac{10.000_mg_Pb}{gram_SRM} \right) \left(\frac{1_flask}{500.00_mL} \right) \left(\frac{1000_ug}{mg} \right) = \left(\frac{40.0_ug_Pb}{mL_solution} \right)$$

Empty Polyethylene bottle mass: _____ grams

Bottle Initial Mass (includes added SRM amount): _____ g

Bottle Final Mass (after SRM transfer to flask): _____ g

**Bottle Initial Mass - Bottle Final Mass = grams of SRM added to
Flask**

Calculation Data (from above)

NIST SRM Certified Value of Lead (in mg/g): _____

Mass of SRM added to flask (g): _____

Flask Volume (milliliters): _____

STOCK SOLUTION CONCENTRATION: _____ ug / mL

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Revision No. 0
Date: March 2009
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